

Highly ordered graphene for two dimensional electronics

J. Hass, R. Feng, T. Li, X. Li, Z. Zong, W. A. de Heer, P. N. First, and E. H. Conrad^{a)}
The Georgia Institute of Technology, Atlanta, Georgia 30332-0430

C. A. Jeffrey

Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211

C. Berger

CNRS-LEPES, BP166, 38042 Grenoble Cedex, France

(Received 26 April 2006; accepted 22 August 2006; published online 3 October 2006)

With expanding interest in graphene-based electronics, it is crucial that high quality graphene films be grown. Sublimation of Si from the 4H-SiC(0001) (Si-terminated) surface in ultrahigh vacuum is a demonstrated method to produce epitaxial graphene sheets on a semiconductor. In this letter the authors show that graphene grown from the SiC(000 $\bar{1}$) (C-terminated) surface are of higher quality than those previously grown on SiC(0001). Graphene grown on the C face can have structural domain sizes more than three times larger than those grown on the Si face while at the same time reducing SiC substrate disorder from sublimation by an order of magnitude. © 2006 American Institute of Physics. [DOI: 10.1063/1.2358299]

An increasingly large effort is underway to create materials suitable for nanometer-scale electronic devices. One proposed avenue is to take advantage of the unique electronic properties of carbon nanotubes (CNTs) to make gated devices and ballistic conducting wires.¹ Challenges for such an approach are control of the properties of individual CNTs (e.g., diameter and helicity), inherent heterojunction impedances associated with interconnection of CNTs, and the assembly of vast networks from individual CNT devices. Similar challenges are inherent to any approach that relies on preformed nanoscale objects. A more conventional means to achieve large-scale integration of nanoelectronic devices would be to rely on the continued scaling of lithographic techniques, which have been the semiconductor industry's greatest feat. Assuming such advances in lithography, a key issue is then the choice of material for nanopatterning. A suitable material should have excellent transport properties (e.g., mobility) and allow for control of electronic properties (band gap and doping) down to nanometer sizes.

It has been proposed that the unique electronic properties of CNTs could be obtained if graphene sheets were limited to nanometer-scale dimensions.² Recent experiments have demonstrated the unique electronic properties of graphene,^{3–5} thus charting a potential route to nanoelectronics based on epitaxial graphene (EG).⁶ A requirement for further progress will be the preparation of a controlled number (thickness) of very large epitaxial graphene sheets on semiconductor substrates. These can be lithographically patterned into narrow ribbons or other shapes, providing the necessary confinement for devices. Thus a scalable assembly of nanopatterned EG devices should be possible, with ballistic graphene conductors as interconnects.

Prior investigations of 6H- and 4H-SiC(0001) and (000 $\bar{1}$) surfaces showed that graphite films can be grown on these surfaces by sublimating Si from SiC during heating above $\sim 1200^\circ\text{C}$ in ultrahigh vacuum (UHV).^{7–9} These studies showed that graphite grows epitaxially on the (0001) Si-

terminated (Si-face) surface of SiC, while graphite grown on the C-terminated (000 $\bar{1}$) (C-face) surface was rotationally disordered and under some conditions formed nanocaps instead of a smooth film.¹⁰ Consequently, the C face was initially overlooked as a potential substrate for graphene-based electronics.

In this letter we report that the classification of the C-face graphite as poorly ordered compared to the Si face is incorrect. We instead show that the mean structural domain size on C-face graphite is much larger than on the Si face and that the inherent substrate roughness from sublimation is dramatically suppressed compared to the best previously reported Si-face films. The improved structural order correlates with recent magnetotransport measurements, which show an order of magnitude improvement in electron mobilities for graphite films prepared on the C face of SiC and coherence lengths exceeding $1\ \mu\text{m}$.¹¹ These observations have important implications for the science and technology of graphene.

All substrates were 4H-SiC purchased from Cree, Inc.¹² Prior to graphitization the samples were ultrasonically cleaned in acetone and ethanol, then hydrogen etched at 1600°C for 30 min. The H_2 etching was done in a vacuum rf-induction furnace with a $200\ \text{cm}^3$ flow of 5% H_2 /95% Ar at ~ 1 atm. This process removed all surface scratches and left a regularly stepped surface, as characterized by atomic force microscopy. A typical step terrace width is $\geq 1\ \mu\text{m}$ with a step height of $5\ \text{\AA}$ (this corresponds to an $\sim 0.03^\circ$ miscut).

Si-face 4H-SiC(0001) samples were prepared in UHV ($P < 1 \times 10^{-10}$ Torr) by electron-bombardment heating. Substrates were first heated to 1100°C for 6 min, then to 1320°C for 8 min to remove surface contamination and form a well-ordered $\sqrt{3} \times \sqrt{3}$ reconstruction. They were subsequently heated to 1400 – 1440°C for 6–12 min to create graphene films of one to two layers thick, as determined by x-ray reflectivity. UHV preparation of C-face samples was found to be problematic, producing small domain sizes and carbon nanocaps. For this reason C-face 4H-SiC(000 $\bar{1}$) samples were prepared by heating to 1430°C for 5–8 min

^{a)}Electronic mail: edward.conrad@physics.gatech.edu

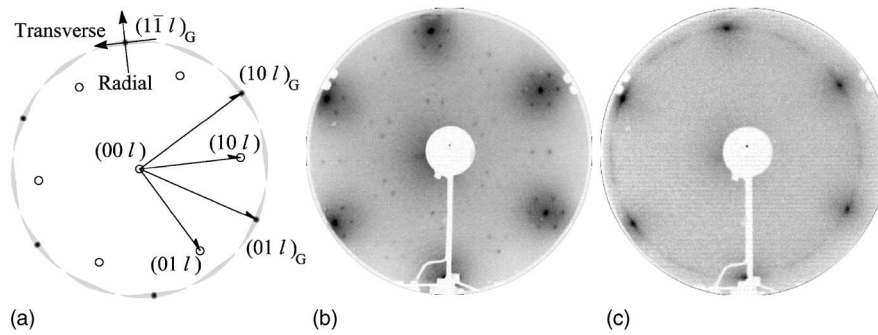


FIG. 1. (a) Schematic of reciprocal space for graphite on SiC. Graphite rods (●) are rotated 30° from the SiC rods (○). Shaded regions represent the effect of orientational disorder in the graphite. Radial and transverse x-ray scan directions for Fig. 2 are depicted in (a). (b) and (c) show LEED images acquired at 75 eV electron energy. (b) A SiC(0001) Si-face surface with two graphene layers (UHV synthesis). (c) SiC(0001) C-face surface with seven graphene layers (induction furnace synthesis).

in a vacuum rf-induction furnace ($P=3 \times 10^{-5}$ Torr). These parameters produced graphitic films of 4–13 graphene layers.

The x-ray scattering experiments were performed at the Advanced Photon Source, Argonne National Laboratory, on the 6ID-B- μ CAT beam line at 16.2 keV photon energy. The graphite film thickness for all samples was determined by measuring the x-ray intensity as function of ℓ along the graphite $(1, \bar{1}, \ell)_G$ rod.⁸ The notation $(h, k, \ell)_G$ identifies a reciprocal-space point in units of the graphite hexagonal reciprocal lattice basis vectors: $a_G^* = 2.9508 \text{ \AA}^{-1}$ and $c_G^* = 1.8829 \text{ \AA}^{-1}$. Unsubscripted reciprocal-space coordinates (h, k, ℓ) refer to the substrate 4H-SiC hexagonal reciprocal lattice units: $a^* = 2.3552 \text{ \AA}^{-1}$ and $c^* = 0.6230 \text{ \AA}^{-1}$.

A reciprocal-space schematic for epitaxial graphene on SiC is shown in Fig. 1(a). Open circles depict the (1×1) low-energy electron diffraction (LEED) pattern from an unreconstructed SiC surface, while the filled circles are the $(1 \times 1)_G$ pattern for a graphene or graphite film with hexagonal unit cell rotated azimuthally by 30° ($R30^\circ$) relative to the SiC (1×1) cell. The diffuse ring through the $(1 \times 1)_G$ graphite spots in Fig. 1(a) represents the (1×1) LEED pattern from a graphene film with rotational disorder relative to the SiC surface.

Figure 1(b) shows the LEED pattern obtained from a two-graphene-layer film grown on the Si face of SiC. In addition to the graphite and SiC (1×1) patterns, it shows a complex $6\sqrt{3} \times 6\sqrt{3}R30^\circ$ reconstruction, which is well known and has been studied extensively in the literature (see, e.g., Refs. 9 and 13 and references therein). The LEED pattern from a C-face sample with seven graphene layers is shown in Fig. 1(c). The LEED only shows the sixfold graphite pattern because the thicker C-face film attenuates the electron beam. The azimuthal streaks in Fig. 1(c) may indicate some rotational disorder in the graphene sheets (as previously observed⁹).

More detailed information on the structural order of the samples was acquired by surface x-ray scattering. We have measured the width of the graphite $(00\ell)_G$ and $(1\bar{1}\ell)_G$ rods on C- and Si-face samples. Figure 2 shows radial scans [see Fig. 1(a)] across the graphite $(1, \bar{1}, 1.5)_G$ crystal truncation rod for both the Si- and C-face samples. The Si-face samples have a radial width of $\Delta q_r \sim 0.022 \text{ \AA}^{-1}$, corresponding to a graphite mean coherent domain size¹⁴ $L = 2\pi/\Delta q_r \sim 290 \text{ \AA}$. This is very similar to the graphite domain size observed by Charrier *et al.*⁸ and is typical of the quality of graphite grown

on the SiC(0001) surface reported to date in the literature. Although their surface treatment was different from ours, the fact that the domain sizes are similar suggests a limit on the graphite quality other than surface preparation.

In contrast, graphite grown on the C-face has much larger domain sizes demonstrated by the smaller radial widths in Fig. 2: $\Delta q_r \sim 0.007 \text{ \AA}^{-1}$, corresponding to $L \sim 900 \text{ \AA}$. So while the LEED patterns show azimuthal disorder in the C-face graphite, the coherent graphite domains are more than three times larger than for the Si-face graphite. This improved structural coherence correlates with the high carrier mobility of $1\text{--}2.7 \text{ m}^2/\text{V s}$ measured recently for the C-face graphene compared to $\sim 0.1 \text{ m}^2/\text{V s}$ for those measured on Si-face graphite films.¹¹ We note that the difference in film thickness may play a role in the long range order of the films. However, the C-face Δq_r do not change for films between 7 and 13 layers. There is also little difference in the long range order of one to two layer graphene films on the Si face. In addition growth of four to five graphene layers on Si face requires temperature above $\sim 1500^\circ\text{C}$, where the substrate disorder becomes problematic (see below).

Why are the C-face graphite films so much better than the Si-face films? While we are not able to explain the details of the growth mechanism leading to this difference, the x-ray data do point out a dramatic difference in the surface morphology of the SiC substrate after film growth. Transverse scans along the specular (00ℓ) rod were taken on both C- and

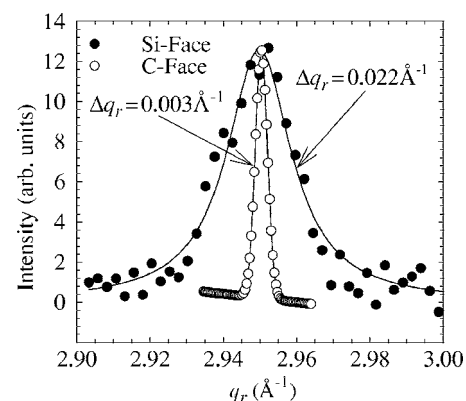


FIG. 2. Radial scans through the graphite crystal truncation rod $(1, \bar{1}, 1.5)_G$ for both two layers of graphene grown on a Si-face sample (●) and seven layers of graphene grown on a C-face sample (○). Solid lines are Lorentzian fits.

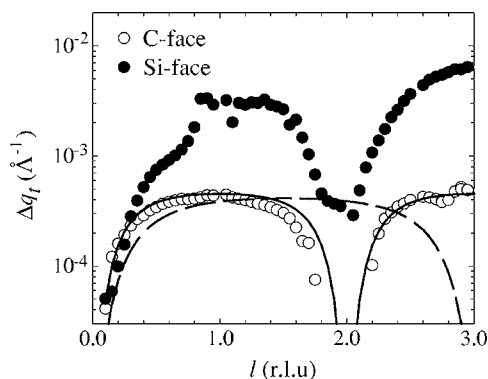


FIG. 3. Comparison of the full width at half maximum (Δq_l) of the $(00\ell)_G$ rod vs $q_z = \ell c_{\text{SiC}}$ from (●) a two-layer graphene film grown on the Si face and (○) an eight-layer film grown on a C-face 4H-SiC substrate. Instrument broadening has been removed for clarification. The lines are fits to a geometric distribution of steps and step heights with either the (solid line) 1/2 4H step height or the (dashed line) graphite step height.

Si-face graphitized surfaces. The transverse peak widths Δq_l are plotted in Fig. 3 versus ℓ (SiC units). These scans reveal a modulation of the width with ℓ that is very different for the C- and Si-face graphitized surfaces. The peak-width modulation is due to atomic steps.¹⁴ In this case it is due to steps on the SiC substrate and not steps in the graphite. We know this for two reasons. First, graphite steps would cause a width modulation of the graphite $(1, \bar{1}, \ell)_G$ rod that is not observed.

Second, the modulation period $\Delta \ell$ is inversely proportional to the step height: $d_{\text{step}} = c_{\text{SiC}} / \Delta \ell$. For both C- and Si-face samples, $\Delta \ell$ corresponds to half of the 4H unit cell height (5.043 Å) and not to the graphite step height (3.337 Å) or any multiple. This is clearly demonstrated by the fits in Fig. 3. The fits are to a model of a geometric distributions of steps and step heights based on either the half 4H unit cell height or the graphite step height. It is clear that the graphite steps produce the wrong period.

The maximum width in Fig. 3 is inversely proportional to the mean distance between steps on the SiC substrate, D , $D = 2\pi / \Delta q_l$.¹⁴ Because the modulation amplitude is much larger for the Si-face sample, we conclude that the SiC step density is more than an order of magnitude greater than on the graphitized C face (we note that the starting SiC step density before graphitization was nearly the same for both samples).

Quantitatively, the C-face samples show that the mean terrace width of the SiC substrate is $D_C \sim 1.4 \mu\text{m}$, while the Si-face samples have a terrace size of $D_{\text{Si}} \sim 0.2 \mu\text{m}$. The higher step densities observed after graphitization on the Si-face substrate correlate with the poorer long range order of the graphite grown on this face. Whether this is a cause or effect relation remains to be determined. We also note that the C-face studies of Kusunoki *et al.*¹⁰ for vacuum furnace grown films showed dense CNT formation for growth tem-

peratures $\sim 1700^\circ\text{C}$ and the formation of nanocaps for temperatures $\sim 1250^\circ\text{C}$. We can speculate that the growth of high quality graphene films on the C face occurs in a tight temperature range near 1430°C . This suggests a delicate balance between sufficient Si evaporation leading to a carbon equivalent graphene density and a sufficiently fast kinetic pathway to graphitize the carbon rich interface without nucleating CNTs.

In conclusion we have shown that ultrathin films of well-ordered graphite (graphene) can be grown on the $\text{SiC}(000\bar{1})$ surface via Si sublimation. In spite of a small orientational disorder, the long range order of the graphite on this surface is more than three times larger than previously reported for graphite grown on the $\text{SiC}(0001)$ surface.

This research was supported by the National Science Foundation under Grant No. 0404084, Intel Research, the Department of Energy (DE-FG02-02ER45956), and the Natural Sciences and Engineering Research Council of Canada to one of the authors (C.A.J.). The Advanced Photon Source is supported by the DOE Office of Basic Energy Sciences, Contract No. W-31-109-Eng-38. The μ -CAT beam line is supported through Ames Lab, operated for the U.S. DOE by Iowa State University under Contract No. W-7405-Eng-82. Any opinions, findings, and conclusions or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the research sponsors.

¹See, e.g., Ph. Avouris, *Acc. Chem. Res.* **35**, 1026 (2002).

²K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus, *Phys. Rev. B* **54**, 17954 (1996).

³K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Nature (London)* **438**, 197 (2005).

⁴K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, *Science* **306**, 666 (2004).

⁵Y. Zhang, Y.-W. Tan, H. L. Stormer, and P. Kim, *Nature (London)* **438**, 201 (2005).

⁶C. Berger, Z. Song, T. Li, X. Li, A. Y. Ogbazghi, R. Feng, Z. Dai, T. Grenet, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, *J. Phys. Chem. B* **108**, 19912 (2004).

⁷A. J. Van Bommel, J. E. Crombeen, and A. Van Tooren, *Surf. Sci.* **48**, 463 (1977).

⁸A. Charrier, A. Coati, T. Argunova, F. Thibaudau, Y. Garreau, R. Pinchaux, I. Forbeaux, J.-M. Debever, M. Sauvage-Simkin, and J.-M. Themlin, *J. Appl. Phys.* **92**, 2479 (2002).

⁹I. Forbeaux, J.-M. Themlin, A. Charrier, F. Thibaudau, and J.-M. Debever, *Appl. Surf. Sci.* **162/163**, 406 (2000).

¹⁰M. Kusunoki, T. Suzuki, T. Hirayama, N. Shibata, and K. Kaneko, *Appl. Phys. Lett.* **77**, 531 (2000).

¹¹C. Berger, Z. Song, X. Li, X. Wu, N. Brown, C. Naud, D. Mayou, T. Li, J. Hass, A. N. Marchenkov, E. H. Conrad, P. N. First, and W. A. de Heer, *Science* **312**, 1191 (2006).

¹²Cree Inc., 4600 Silicon Drive, Durham, NC 27703.

¹³T. Li, Ph.D. thesis, Georgia Institute of Technology, 2006.

¹⁴T. M. Lu and M. G. Lagally, *Surf. Sci.* **120**, 47 (1982).